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MOLECULAR STRUCTURE OF OZONE

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The Infrared Absorption Spectrum and the Molecular Structure of Ozone

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Of the seven known infrared absorption bands of ozone, four (4.7μ , 7.39μ , 9.6μ , and 11.38μ) have been investigated for the first time with a grating spectrometer. The band at 4.7μ shows three branches, not very sharply defined, while the one at 7.39μ shows only a single peak. The strongest band, at 9.6μ , has been resolved into two main branches which probably belong to two different vibrations. The band at 11.38μ has been tentatively ascribed to nitrogen pentoxide, which often occurs as an impurity in ozone. Three fundamental vibrational frequencies, *viz.*, 528 cm^{-1} , 1033 cm^{-1} , and 1355 cm^{-1} , have been selected from the observational data. The rotational fine structure could not be completely resolved; it appears to have the irregularity characteristic of an asymmetrical rotator. The envelopes of the four observed bands have been completely mapped out. The infrared absorption spectrum of ozone is discussed and it is shown that the molecule cannot have the form of a straight line nor an equilateral triangle but it is probably represented by an isosceles triangle where the angle at the apex is less than 60° . By making use of these assumptions it was possible to order the observed frequencies in a fashion consistent with their envelopes. This general shape of isosceles triangle is the only one allowed by the observational data; the other shape of isosceles triangle, with apex angle greater than 60° , is ruled out.

DURING the past ten years ozone has attracted considerable interest and many attempts have been made to determine its structure. It is one of the few triatomic molecules whose infrared absorption spectrum has not heretofore been investigated with the high dispersion of a grating spectrometer. It is true that very many data have been collected on its absorption bands in the photographic region of the spectrum, but from these it has not been possible as yet to give a satisfactory description of its molecular structure.

John Tyndall¹ in 1872 discovered that ozone absorbs infrared radiation and, in 1904, K. Angstrom² first measured its infrared absorption spectrum. With low concentrations of ozone he found bands at 4.8μ , 5.8μ , 6.7μ and 9.6μ .

A more thorough investigation of the ozone absorption in this region was carried out by E. Ladenburg and E. Lehmann³ in 1906. By using a more efficient method of preparation they were able to observe it in higher concentrations and consequently found some weaker bands which Angstrom had missed. They found bands at 1.1μ , 3.7μ , 4.8μ , 5.9μ , 6.6μ , 7.6μ , 9.9μ and 11.35μ . Of these, the one at 5.9μ was later shown by E. Warburg and G. Leithauser⁴ to be due to nitrogen pentoxide.

¹ John Tyndall, *Contributions to Physics in the Domain of Radiant Heat*, London (1872).

² K. Angstrom, *Arch. f. Mat., Astron., och Physik* **1**, 347, 395 (1904).

³ E. Ladenburg and E. Lehmann, *Ann. d. Physik* **21**, 305 (1906).

⁴ E. Warburg and G. Leithauser, *Ann. d. Physik* **23**, 209 (1907). See also another paper by these same two investigators, *Ann. d. Physik* **28**, 313 (1909).

Quite recently A. Jakowlewa and V. Kondratjew⁵ made measurements on some of the ultraviolet electronic bands of ozone. They concluded from the results of their own measurements and those of others that ozone is a linear molecule, but this is not in agreement with our conclusions, as will be shown later.

EXPERIMENTAL

The classical and most common method of preparing ozone is one using a Siemens' ozonizer, in which a silent electric discharge is passed through air or oxygen. This gives only a low yield; the exit gases contain at best only about 10 percent of ozone.

A more efficient method of preparing ozone, described by A. K. Brewer and J. W. Westhaver⁶ was used in the present investigation. In this method a glow discharge is maintained in oxygen while the discharge tube is immersed in liquid air. Under these conditions liquid ozone condenses out on the walls of the discharge tube. Practically pure ozone gas may be obtained by distilling the liquid ozone thus formed. This last procedure, the distillation of the liquid ozone, was a hazardous one in spite of the fact that all organic matter was excluded from the entire system. On four different occasions the discharge tube exploded violently during the course of the distillation.

The absorption cells were glass tubes 4.5 cm in internal diameter and 25 cm and 1 m in length, respectively. Rocksalt windows were fastened on the ends by means of a thin, quick-drying lacquer. This method of fastening the windows had the advantage of enabling one to remove them when necessary by merely soaking in acetone or wood alcohol, thus avoiding the application of heat. The ozone was kept in the cells at atmospheric pressure by means of traps filled with phosphoric acid.

The spectrometer was of the usual type employing a rocksalt prism as a monochromator for the radiation falling on the grating. The thermocouples were very kindly supplied by Dr. J. D. Hardy. They were of the Pfund design and were connected to the familiar type of Moll relay, where the deflections of the first galvanometer were amplified. The aperture throughout the spectrometer was f5. A 25 cm parabolic mirror of 120 cm focal length was used in front of the grating. The slit widths used for each band are indicated in Fig. 1. With 0.88 ampere passing through the Nernst glower, which was used as a source, and the lamp in the Moll relay operating at 2.83 volts a deflection of about 70 mm was obtained at 9.6μ through the empty cell, and with a slit width of 0.3 cm^{-1} . Two gratings were used, with 1440 and 1200 lines per inch, respectively. The calibrations were obtained from charts previously prepared for them by means of standard infrared lines.

On account of the difficulty and hazard involved in handling highly concentrated ozone no attempt was made to perform a quantitative analysis of the contents of the absorption cell. It was, however, possible to make a

⁵ A. Jakowlewa and V. Kondratjew, *Phys. Zeits. d. Sowjetunion* **1**, 471 (1932).

⁶ A. K. Brewer and J. W. Westhaver, *J. Phys. Chem.* **34**, 1280 (1930).

rough estimate of the amount of ozone in the cell from considerations of the general behavior of the preparation.

The results of the investigation are shown in Fig. 1 as a group of curves giving the envelopes of the four different absorption bands studied. Most of the envelopes shows persistent irregularities, which indicate that the resolving power of the spectrometer was almost great enough to reveal the fine structure. It seems probable not only that the fine structure lines observed are real but also that they are distributed in the irregular manner which is characteristic of the asymmetrical rotator. This point will be discussed later.

The 9.6μ band was investigated with both the meter cell and the 25 cm. cell. Curve I was taken with practically pure ozone gas at atmospheric pres-

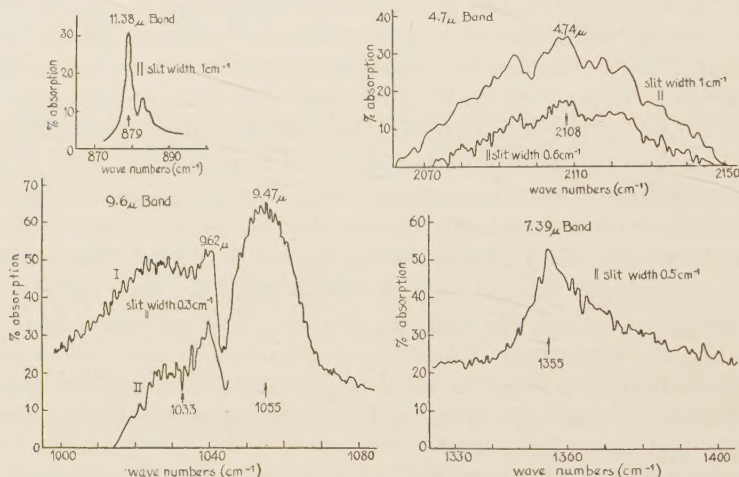


Fig. 1.

sure in the shorter cell, and curve II with a very low concentration in the meter cell. This band has apparently three branches. The one on the high-frequency side of the center (9.62μ) is the strongest, and the one on the low-frequency is the weakest of the three. The low-frequency branch becomes weaker than the other two at low concentration. The high-frequency branch was not studied in detail at low concentrations but a few readings taken at 9.47μ at the same time curve II was taken showed an absorption of about 48 percent, showing that this branch remained the strongest of the three. This behavior indicates that the high-frequency branch may be associated with one fundamental frequency, and the rest of the band with another.

The 7.39μ band lies in a region where the absorption due to water vapor is very noticeable. It also was observed with the same high concentration of ozone in the 25 cm cell that was used in obtaining curve I for the 9.6μ band. The curve shown for this 7.39μ band represents the average of two separate and consistent sets of data taken under the same conditions. The high background on each side of the strong single branch might be fictitious on account of the uncertainty in calculating the percentage absorption in a region where

water vapor absorbs as strongly as it does here. However, it is stronger than the 4.7μ band, which could not be detected under the same conditions.

The bands at 9.6μ and at 7.39μ are the two strongest ones; the others were looked for but could not be detected with the same concentration of ozone in the 25 cm cell.

The two curves shown for the 4.7μ band were obtained with two slightly different ozone concentrations in the meter cell, and also with different slit widths, as indicated in Fig. 1.

The small single peak of absorption at 11.38μ was observable only with very high concentrations of ozone in the meter cell. The curve shown for it was obtained with a higher concentration of ozone in the meter cell than was used to obtain the 4.7μ band, in fact it was not observable under the conditions which yielded the curves for the 4.7μ band.

In the first two columns of Table I is a summary of the wave-lengths and relative intensities of the absorption maxima of ozone obtained in this in-

TABLE I.

Wave-lengths	Relative intensities	Ladenburg and Lehmann	
		Wave-lengths	Relative intensities
—	—	1.1μ	1
—	—	3.7	2
4.74μ	5	4.7	5
—	—	6.6	2
7.39	7	7.7	3
9.47	10		
9.62	8	9.9	10
11.38	2	11.3	3

vestigation. In the last two columns are given the values reported by Ladenburg and Lehmann,³ it is seen that there is very satisfactory agreement between these two sets of results, considering the fact that Ladenburg and Lehmann used a prism spectrometer.

The weak band at 11.38μ does not fit with the other observed bands into any scheme of frequencies. It may possibly be due to nitrogen pentoxide, which has a very strong band at 5.75μ , for the band at 5.75μ may be the first overtone of a fundamental at 11.38μ .

Several attempts were made to find the Raman spectrum of liquid ozone, using pure ozone as well as solutions of ozone in liquid oxygen. The details of these attempts have already been published.⁷ The extreme faintness of the doublet observed, corresponding to a mean frequency shift of 1280 cm^{-1} (7.81μ), and the fact that this frequency does not fit in with the infrared frequencies makes it doubtful whether it is real.

THEORETICAL

§1

The data obtained in this investigation of the infrared absorption bands of ozone are not as complete as might be desired. In the first place its insta-

⁷ G. B. B. M. Sutherland and S. L. Gerhard, *Nature* **130**, 241 (1932).

bility caused several explosions and made the gathering of data expensive and difficult, and in the second place the rotational fine structure is so closely spaced that it was not possible to resolve it. It is therefore necessary in the interpretation of the data to approach the subject from a rather general point of view and this requires the discussion of all the possible models for its structure. It will be shown that the data are consistent with only one model, and that furthermore this model has certain other properties similar to the known properties of ozone.

The frequencies observed for ozone have been satisfactorily correlated in the following way. The single band at 1355 cm^{-1} is taken as the first fundamental frequency, ν_1 , then the band at 2710 cm^{-1} , reported by Ladenburg and Lehmann, is its first harmonic, $2\nu_1$. The strong band at 1055 cm^{-1} is assigned to the first overtone of a fundamental ν_2 , at 528 cm^{-1} , which could not be observed because of the high absorption of the rocksalt windows in this region. The minimum at 1033 cm^{-1} is taken as the center of a doublet type band representing the third fundamental frequency, ν_3 . The 2108 cm^{-1} band may be called $2\nu_3$; it is apparently multiple and contains other combinations as well. The weak band reported by Ladenburg and Lehmann at 1515 cm^{-1} may very well be the combination $\nu_2 + \nu_3$. Except for the 11.38μ band, which is ascribed to nitrogen pentoxide, all the known bands of ozone are thus accounted for. There are three fundamental frequencies represented. The fundamental of two of them and the first harmonics of all three have been observed, as well as several combinations.

These bands display different kinds of envelopes. The fundamental, ν_1 at 1355 cm^{-1} , has certainly a zero branch type of envelope, with the zero branch very strong in comparison with the positive and negative branches. The $2\nu_2$ band, at 1055 cm^{-1} , has also a zero branch type of envelope, while that for ν_3 , at 1033 cm^{-1} , is of the doublet type. The envelope for $2\nu_3$, at 2108 cm^{-1} , is apparently of the zero branch type. Unfortunately the envelopes of the remaining bands of ozone have not been observed, however, it will be possible to gather from the data in hand sufficient information to decide on the shape of the molecule.

For a triatomic molecule, such as ozone, there are three plausible shapes, *viz.*, linear, equilateral triangle and isosceles triangle. The three atoms of oxygen making up the ozone molecule need not all be alike; the force fields and electron configurations may not be the same for all the atoms. The possibilities of these three types of structure will now be discussed in connection with the data obtained and with the aid of the results of the wave mechanical analysis of infrared spectra given in a recent paper by D. M. Dennison.⁸

§2

There are two possible linear models for ozone, a symmetrical one, with the three atoms symmetrically arranged along a line, as is the case in carbon

⁸ D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

dioxide, and an unsymmetrical one. The symmetrical type of linear molecule would display absorption bands resembling those of carbon dioxide. It would have similar vibrational properties and would obey the same selection rules, namely, that combinations or overtone frequencies which are the sum of any two observed frequencies cannot occur.⁸ These conditions are not met by the frequencies observed for ozone, *viz.*, the band at 2108 cm^{-1} has twice the frequency of the 1033 cm^{-1} band, and the one reported at 2710 cm^{-1} has twice the frequency of the 1355 cm^{-1} band. With 528 cm^{-1} as a fundamental the band reported at 1515 cm^{-1} is assigned to the combination $1033 + 528$. The occurrence of these overtones and combinations is definitely in disagreement with the requirements for a linear symmetrical model and is sufficient to rule it out as a possible structure for ozone.

The other possible linear model would resemble the molecule of nitrous oxide, NNO. The selection rules for this model allow three active fundamental frequencies and all possible combinations and overtones. The vibration-rotation bands consist of fine structure lines regularly spaced in frequency.⁹ There are two types of bands, both having essentially similar positive and negative branches, the one having a strong zero branch and the other none. When the ozone bands are examined it is found that none of them have regularly spaced fine structure lines. The positive and negative branches of the several bands do not stand out distinctly as they do in the case of nitrous oxide. There is no similarity between even the general outlines of the envelopes of any two bands. If ozone were this unsymmetrical linear type of molecule, then the positive and negative branches of the 1033 cm^{-1} and 1355 cm^{-1} (fundamental) bands should be similar and should have almost equal doublet spacings, but this is obviously not the case. These fundamental differences between the observed bands of ozone and those to be expected from linear molecules make it evident that the ozone molecule cannot be a linear one.

§3

In the isosceles triangle model for ozone the oxygen atom at the apex is taken to be different from the two at the base. The general solution of the vibrational problem has already been given by several investigators.^{10,11} Three fundamental frequencies are to be expected for the general isosceles triangle. According to the conventions adopted in labelling these frequencies the electric moment vibrates along the Y axis (*i.e.*, the bisector of the apex angle) for the frequencies ν_1 and ν_2 , where $\nu_1 \geq \nu_2$, and along the X axis (which is perpendicular to the Y axis) for the frequency ν_3 .

In specializing to the equilateral triangle all three atoms become identical. In this case the frequency ν_1 is certainly inactive, since it corresponds to a motion in which all the atoms vibrate along the bisectors of their respective (apex) angles with the same amplitude and in the same phase with respect

⁹ E. K. Plyler and E. F. Barker, *Phys. Rev.* **38**, 1827 (1931).

¹⁰ N. Bjerrum, *Verh. d. Deut. Phys. Ges.* **16**, 640, 737 (1914).

¹¹ D. M. Dennison, *Phil. Mag.* **1**, 195 (1926).

to the center of gravity of the molecule. The two frequencies ν_2 and ν_3 become equal, thus forming degenerate states. Whether or not the frequency ν_2 would also be inactive depends upon the interaction of the electron clouds surrounding the three nuclei when they execute this normal vibration. It is conceivable that at one extreme displacement in this vibration the electrons surrounding the two lower nuclei could so repel those surrounding the upper nucleus that the center of the negative charges would lie above the center of the positive charges, thus producing a change in the electric moment of the molecule. Even if it were active it is very likely that it would be comparatively weak because of the relatively small amplitude of the oscillating electric doublet.

If ozone were this type of molecule it should be possible to correlate all the observed bands with only two fundamental frequencies, and one of these should be inactive. On the contrary the bands observed for ozone cannot be arranged in any scheme with only two fundamental frequencies unless very low frequencies are chosen and the observed bands ascribed to combinations and high multiples of them. This sort of procedure is evidently unreasonable in view of the simple relations existing between the frequencies observed for substances heretofore investigated. It takes three fundamental frequencies to account for all the ozone bands, and these three all appear to be active. This is very strong evidence against the equilateral triangle as the correct model for ozone.

Another source of evidence which is equally important is the almost complete absence of the Raman spectrum of ozone. Up to the present it has been observed that molecules possessing a highly symmetrical configuration, which results in an inactive vibrational frequency, have fairly strong Raman spectra, as in the cases of carbon dioxide and carbon tetrachloride. On the other hand it has also been found true that molecules lacking an inactive frequency, such as water, have a weak Raman spectrum.¹²

§4

The solution of the vibration problem for the isosceles triangle model has already been described. There are three different and active fundamental frequencies. The question of the overtones of these frequencies has been discussed by Dennison,⁸ who showed that in general they would all be active. If the overtone is represented by $\nu = n_1\nu_1 + n_2\nu_2 + n_3\nu_3$ the change of the electric moment is along the Y axis for even values of n_3 and along the X axis for odd values.

The shapes of the envelopes of the bands at these various vibrational frequencies will depend upon the direction of the change of the electric moment with respect to the principal axes of inertia. If in the case of ozone the apex angle is less than 60° , then the axis of least moment of inertia, A , will be along the Y axis, and the axis of middle moment of inertia, B , will be along the X axis.

¹² These results have recently been justified and explained on a theoretical basis by Placzek, *Zeits. f. Physik* **70**, 84 (1931).

The axis of greatest moment of inertia, C , is perpendicular to the plane of the figure. No changes of electric moment can ever lie along this axis because no vibrations can take place outside the plane of the triangle. Thus in the general overtone $n_1\nu_1 + n_2\nu_2 + n_3\nu_3$ the change of electric moment will lie along the A axis for even values of n_3 and along the B axis for odd values.

On the other hand, if the apex angle in the case of ozone were greater than 60° the inertial axes A and B would be interchanged, and then in the general overtone the change of electric moment would be along the B axis for even values of n_3 and along the A axis for odd values.

According to Dennison⁸ the envelopes of the bands produced by vibrations of the electric moment along the least axis of inertia should show a decided zero branch, while those produced by vibrations along the middle axis of inertia should show a doublet structure.

Whatever the disposition of the axes of inertia may be in the molecule the two frequencies ν_1 and ν_2 will have the same kind of envelopes, and ν_3 will have a different kind. If only one fundamental frequency displays the doublet type of envelope, then the apex angle is less than 60° , whereas if only one of the fundamental frequencies displays a zero branch, then the apex angle is greater than 60° .

When the envelopes of the ozone bands are examined it becomes evident that they can be very nicely arranged to fit the requirements for an isosceles triangle with the apex angle less than 60° . In Table II is given a comparison

TABLE II.

Wave-lengths	ν_i	Frequencies		Type of envelope	
		observed	Calculated	Observed	Predicted
(18.9 μ)*	ν_2	—	528 cm ⁻¹	—	Z
9.67	ν_3	1033 cm ⁻¹	—	D	D
9.47	$2\nu_2$	1055	—	Z	Z
7.39	ν_1	1355	—	Z	Z
6.6†	$\nu_2 + \nu_3$	1515	{ 1561	—	D
	$3\nu_2$		{ 1584		Z
	$2\nu_3$		{ 2066		Z
4.7	$2\nu_2 + \nu_3$	2108	{ 2088	{ Z	D
	$4\nu_2$		{ 2110		Z
3.7†	$2\nu_1$	2710	2710	—	Z

* This band was not looked for, because it is in a region where the absorption due to the rocksalt windows on the cell made observations impossible.

† Reported by Ladenburg and Lehmann. The wave-lengths are not known as accurately as those of the other bands and nothing is known about the envelopes.

of the observed envelopes and those predicated for ozone on the basis of the isosceles triangle model. In the last two columns D stands for doublet type and Z for zero branch type of envelope.

The fundamental ν_1 displays a zero branch type of envelope, with very weak positive and negative branches; the same holds true for $2\nu_2$. The envelope for ν_3 is of the doublet type, while that for $2\nu_3$ is of the zero branch type, as it should be for even values of n_3 if the apex angle is less than 60° . The observed envelope for the combination $2\nu_2 + \nu_3$ is somewhat obscured by the envelopes of the overtone bands in its immediate vicinity, but the shape

of the whole envelope does not rule out the possibility of a doublet type envelope for this particular combination frequency.

The types of the envelopes of the bands observed show that ozone has the shape of an isosceles triangle with the apex angle less than 60° . This is proven by the occurrence of the zero branch type of envelope for ν_1 and $2\nu_2$. If the molecule were to be represented by an isosceles triangle with an apex angle greater than 60° , then ν_1 and $2\nu_2$ would have the doublet type of envelope and ν_3 would have the zero branch type of envelope. The preponderance of zero branch type over doublet type envelopes in the bands observed for ozone indicates that it has the shape of an isosceles triangle with the apex angle less than 60° . Except for the unknown envelopes of other combinations and overtones the observed data for ozone agree very well with the predictions for this model. The ordering of the ozone data under this scheme may not be unique, but it is a self-consistent one. Other ways of allotting the observed frequencies are possible, but they must all fulfill the requirements of the types of envelopes for the various frequencies.¹³

CONCLUSIONS

The experimental data for ozone have been critically compared with the theoretical predictions for various possible models and also with the data for certain molecules of known structure.

The combination and overtone frequencies observed in the ozone spectrum do not obey the selection rules for a linear symmetrical molecule. The envelopes of the bands and the lack of regularly spaced rotational fine structure lines are not in agreement with those to be expected of a linear unsymmetrical molecule. The equilateral triangle is very definitely ruled out because the frequencies observed for ozone do not obey the requirements that for an equilateral triangle there should be only one active fundamental frequency, and only two fundamental frequencies in all. In addition to this, ozone displays a very weak Raman spectrum, while a highly symmetrical molecule in the form of an equilateral triangle should certainly have a strong Raman spectrum.

The data for ozone do meet the requirements for the isosceles triangle model. There is the correct number of active fundamental frequencies, *viz.*, ν_1 at 1355 cm^{-1} , ν_2 at 528 cm^{-1} , and ν_3 at 1033 cm^{-1} . Overtones and combinations of these fundamental frequencies are also observed. Each fundamental shows its first overtone, and ν_2 apparently displays its second and third overtones. The assignments given the fundamental frequencies thus form a self-consistent scheme, and the calculated frequencies are in fairly good agreement with the observed frequencies. The types of envelopes, zero branch or doublet type, predicted for the fundamental frequencies and the various combinations and overtones appear in the observed bands for the proper fre-

¹³ The case of the oblique triangle has not been discussed since it appears to be so improbable on general grounds. Such a model would, however, have much the same vibrational and rotational properties as an isosceles triangle, except that the direction of change of electric moment would no longer be so simply related to the orientation of the principal axes of inertia.

quencies. On the whole, the observed data for ozone fulfill the requirements for an isosceles triangle with the apex angle less than 60° .

The writer gratefully acknowledges Professor D. M. Dennison's many helpful suggestions in the interpretation of the experimental data, and the generous cooperation of the various members of the Physics Department who made possible the completion of this work.

